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The effects of water on biodiesel production and refining technologies: A review

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ABSTRACT

Presence of water during biodiesel production and purification processes, storage and use in compression ignition (diesel) engines causes problems that cannot be ignored. These problems include: difficulties in biodiesel processing especially during alkali-catalyzed transesterification process, deterioration of biodiesel quality, decrease in heat of combustion, corrosion of fuel system components, and acceleration of hydrolytic reaction. Beside use of water during biodiesel purification results in wastewater discharges which causes environmental effects, due to high contents of chemical oxygen demand, biological oxygen demand, and higher pH values. Thus, this study critically analyzed and examined the effects of water on biodiesel production and the refining of crude biodiesel. Furthermore the effects of water on the quality of biodiesel were also examined.

Contents

1. Introduction

The development of biodiesel as an alternative fuel to supplement or replace petro-diesel is receiving great attention among researchers and policy makers for its numerous advantages such as renewability, biodegradability and lower gaseous emission profile. Also, concerns over increasing energy demand, continuous global warming effects, declining petroleum reserves, petroleum price hike and scarcities have raised the need to search for alternative renewable fuels [1–5]. The annual rate of the global primary energy demand is estimated to increase to a value of 1.7% and reach a value of 16,487 Mtoe from 2002 to 2030 [6]. Thus use of renewable energy is expected to improve the energy availability. Besides renewable energy is one of the most efficient routes to achieve sustainable development [7,8]. Presently several investigations are being conducted on renewable energy such as wind, geothermal, water and biofuels. In recent times, biodiesel is considered to be

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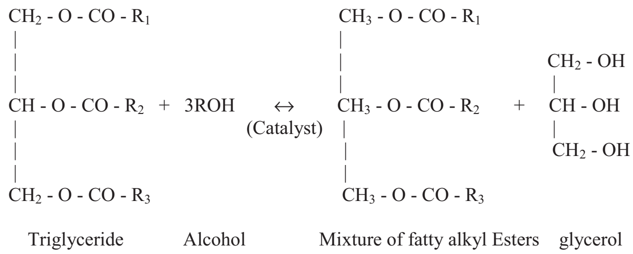


Fig. 1. Transesterification of triglycerides to alkyl esters (biodiesel).

among the best available energy source to come to the forefront [9,10]. Biodiesel is entirely produced from vegetable oils and animal fats. It is environmentally benign and does not contain sulfur, aromatic hydrocarbons, metals or crude oil residues [11]. Thus, it can lower the net greenhouse gas emissions from the transportation sector and reduce the mass and carcinogenicity of particulate matter emissions [12]. Also, biodiesel has recently become more attractive due to its environmental benefits [13,14].

In addition, the struggle against climate change and fossil energy depletion has compelled humanity to decarbonize the economy. The global CO_2 emissions have to be reduced to at least 85% by the year 2050 and most likely by over 95% in developed countries [15]. Moreover the European Union target by 2020 to reduce 20% greenhouse gas emissions, increase the share of renewable energy to 20% and also achieve 20% improvement in energy efficiency [16].

Biodiesel is produced through different techniques such as direct/oil blends, microemulsion, pyrolysis and transesterification [17]. However, the most notable way to produce biodiesel fuel is through transesterification reaction [18–22]. Transesterification is the reaction of triglycerides to fatty acid alkyl esters (FAAE) and low molecular weight alcohols such as methanol and ethanol in the presence of catalyst [11,23,24] as shown in Fig. 1. Methanol is the most favored alcohol because it is less costly and easily obtainable [25]. Transesterification reaction is catalyzed by either homogeneous catalyst (sodium hydroxide, potassium hydroxide, sulfuric acid, hydrochloric acid, etc.) or heterogeneous catalyst (enzymes, alkaline earth metal compounds, titanium silicates, anion exchange resins, guanidine heterogenized on organic polymers, etc.) [3,5,16]. The conversion of triglyceride is usually a stepwise process, it is converted to diglyceride, monoglycerides and finally to glycerol, with 1 mol of esters being librated at each stage [25].

Conventionally, alkali catalyst, such as sodium and potassium hydroxides, is the most preferred catalysts in biodiesel production [26]. The use of alkali catalyst requires high-quality raw materials with free fatty acids (FFAs) not more than 3 wt.%. Above this FFAs requirement, pretreatment is necessary prior transeterification process [25]. However use of refined raw materials containing low FFAs content could amount to 60–80% cost of biodiesel production. The high cost of refined raw materials is considered to be the main obstacle of commercializing biodiesel production [27,28]. Presently low quality raw materials containing high contents of FFAs and water such as waste cooking oils, animal fats and non-edible oils are being explored with the aim of reducing the cost of biodiesel production [29]. However biodiesel production via alkali-catalyzed transesterification reaction is being negatively affected, if the reaction is conducted using raw materials with high water content. This is because water hydrolyzes fatty acids yielding high FFAs contents. The FFAs formed reacts with alkaline catalyst to form soap, which renders separation and purification of biodiesel difficult and costly. Moreover soap formation deactivates the catalyst activity, thus lowering the yield of biodiesel produced [30]. For this reason, heterogeneous catalysts such solid acid catalyst, solid alkaline catalyst and enzymes catalyst are being developed to overcome these problems. Heterogeneous catalyst presents several advantages over homogeneous catalysts such as: easy separation of glycerol, catalyst reusability, high glycerol purity, less amount of wastewater, and low energy and water consumption [25,31]. Even though, the cost of heterogeneous catalyst such as enzymes catalysts is high. But it could be mitigated through immobilization of the enzymes [32].

After transesterification, biodiesel product comes with contaminants that have to be removed before the fuel is used in diesel engines. The removal of by-product, glycerol is the first step usually carried out. This is mostly done through different separation techniques such as: decantation, sedimentation, filtration and centrifugation [30]. After glycerol is removed from biodiesel, vacuum distillation or flash evaporation is employed to remove the residual alcohol. Biodiesel is then water wash and centrifuge to remove catalyst, soap and traces of glycerol. The remaining biodiesel water content is then driven off by means of an evaporator or a vacuum drier. Finally, biodiesel is stored and then distributed to be sold [26].

Thus, the main objective of this paper is to evaluate the effects of water on biodiesel production, refining of crude biodiesel and biodiesel quality.

2. Effects of water on transesterification reaction

During transesterification reaction, presence of water/moisture reduces the conversion of triglycerides to biodiesel fuel. Therefore, it is essential to minimize the water content in the feedstocks prior to transesterification process [33]. Ma et al. [34] noted that during transesterification reaction, presence of water causes larger negative effect than FFAs. Similarly, Demirbas [35] reported that water content is an important factor in the conventional catalytic transesterification of vegetable oils. Canakci and Van Gerpen [28] were of the opinion that presence of water as little as 0.1 wt.% during transesterification reaction will reduce the formation of fatty acid alkyl esters. In the same way, Kusdiana and Saka [36] stated that conversion of triglycerides to methyl esters can be reduced to 6% when only 5% of water is added. The authors also noted that addition of water as little as 0.1 wt.% might lead to the reduction in the yield of methyl esters.

Furthermore, Fangrui et al. [37] stated that even refined oils and fats contain small amounts of FFAs and water. Presence of water speeds up hydrolysis of triglycerides and increases FFAs content in vegetable oils [38]. Table 1 presents the effects of water on biodiesel yields. As earlier stated, during alkali-catalyzed transesterification, FFAs and water create negative effects, since the occurrence of FFAs and water causes formation of soap, consumes the catalyst, reduce its catalytic effectiveness, and results in low conversion and low yields. But, transesterification reaction via alkaline catalyst is the most preferred technique for biodiesel production, because higher conversion of triglycerides to biodiesel above 98% can be achieved using moderate conditions. Besides the reaction is faster and is easily carried out when refined raw materials are used.

2.1. Effects of water on catalyzed transesterification reaction

Catalysts play a significant role in improving production of biodiesel fuel. The choice of catalyst is mostly controlled by the nature of raw material to be used. The performance of acid and alkaline catalysts is usually affected by FFAs and water contents of the raw materials [21]. In the case of heterogeneous (solid and enzymes) catalysts, the effects of water and FFAs contents are less noticed during transesterification process. However the reaction rates are slower [25]. Table 2 presents the effects of water on the performance of different catalysts.

Moreover, the effects of water on catalyzed and non-catalyzed transesterification reaction are discussed as follows.

Table 1
Effects of water on the yields of biodiesel produced from different modes of transesterification reaction.

Vegetable oil	Water content (wt.%)	Yield of methyl esters (wt.%)					Reference
		Alkali catalyst	Acid catalyst	SCM	Solid catalyst	Enzyme catalyst	
Waste cooking oil	5.0	79.5	6.2	100	–	–	[35]
Jatropha oil	0.5	–	–	–	–	92	[32]
Palm oil	2.1	94.4	97.8	98.9	–	–	[38]
Used frying oil	0.2	94.1	97.8	96.9	–	–	[38]
Waste palm oil	>61.0	No reaction	No reaction	95.8	–	–	[38]
Waste frying oil	<0.3	98	–	–	–	–	[39]
Waste cooking oil	1.9	–	–	–	85.3	–	[40]
Waste cooking oil	0.5	–	–	–	91.7	–	[40]
Capparis deciduas oil	2.0	65	–	–	–	–	[41]
Sesbania sesban oil	2.0	29	–	–	–	–	[41]
Waste cooking oil	5.30	78.5	–	–	90	–	[42]
Jatropha oil	0.5	–	–	–	–	92	[43]
Soybean oil	4–30	–	–	–	–	80–90	[44]
Soybean oil	5.8	–	–	–	–	92.2	[45]
Soybean oil	2.8	95	–	[46]	–		
Jatropha oil	5	–	–	–	–	98	[47]
Waste bleaching earths	75	–	–	–	–	50	[48]

Table 2
The effects of water on the performance of different catalysts.

Catalyst type	Presence of water	Performance of catalyst	Reference
Alkaline catalyst	Presence of water	Causes soap formation, consume catalyst, and reduce its catalytic effectiveness	[21,35,49–54]
Acid catalyst	Presence of water low	Performance of the catalyst, better performance than base catalyst	[49,55]
Solid			
Basic solid catalyst	Presence of little water	Catalytic activity was maintained, considerable leaching effects, and continuous catalytic deactivation	[56–62]
Acidic solid catalyst	Presence of water	High catalytic performance Catalyst performance was maintained	[63–66]
Zeolites	Presence of water	High catalyst performance	[3]
	Presence of less amount of water	Better catalyst performance	[67,68]
Enzymes	Presence of water	Less effects on catalyst performance, positively impacted the catalyst performance, high performance, good performance, the catalyst was not inactivated	[45,48,69–72]

2.1.1. *Effects of water on alkali-catalyzed transesterification reaction*

Conventionally, biodiesel production via transesterification is mostly catalyzed by metal hydroxides such as NaOH and KOH and metal alkoxides such as CH_3ONa and CH_3OK [73]. Alkali-catalyzed transesterification reaction usually takes place 4000 times faster than acid-catalyzed transesterification [70]. Singh and Singh [14] reported that for an alkali-catalyzed transesterification, the glycerides and alcohol must be anhydrous. The reaction requires high-quality feedstock with water content less than 0.06 wt.% [74–76]. This makes alkaline catalyst such as metal alkoxides (CH_3ONa and CH_3OK), unsuitable for typical industrial process [21]. According to Kusdiana and Saka [36], conversion of triglycerides via alkaline-catalyzed method is slightly reduced when more water is added. For high-quality feedstocks, Chew and Bhatia [67] stated that at low molar concentration (0.5 mol%), alkaline metal alkoxides could give high biodiesel yield (above 98%) in short reaction times (30 min). Furthermore metal alkoxides could provide higher biodiesel yields than metal hydroxides. It was also observed by Fangrui et al. [37] that sodium hydroxide and sodium methoxide can react with moisture and carbon dioxide in the air, hence decreasing their catalytic effectiveness. As well, sodium and potassium hydroxides can react with alcohol to give water. This reaction is naturally undesirable, because water can react with triglycerides, fatty acids, or esters in hydrolysis reactions [39].

In another study, Jitputti et al. [63] reported that during alkaline metal hydroxide-catalyzed transesterification, even if a water-free vegetable oil and alcohol are used, water is produced from the reaction of the hydroxide and alcohol. Thus alkali-catalyzed transesterification are greatly affected by the presence of water which makes the reaction partially change to saponification, leading to soaps formation [14,77]. Also, Haas [78] noted that water inhibits transesterification reactions since it competes with the alcohol (reactant), thereby transforming the required ester transfer reaction into ester hydrolysis, leading to formation of FFAs. The formed FFAs favor the formation of soap as shown in Fig. 2. Saponification reaction is usually referred to as a side reaction that occurred during transesterification of fats and oils to biodiesel causing soaps formation. Soaps formation increases loss of methyl ester to glycerol phase, resulting to high purification costs and less biodiesel yield [79]. For this reason processing low quality feedstocks containing considerable amount of water and FFAs using alkali-catalyzed route requires the feedstocks to undergo pretreatment via esterification reaction using acid catalyst (H_2SO_4) as shown in Fig. 3. The product (refined feedstocks) obtained with less FFAs content (≤3 wt.%) and water content (<0.06 wt.%) is then used for alkali-catalyzed transesterification to produce biodiesel. Furthermore Velasquez-Orta et al. [80] have produced biodiesel via alkaline in situ transesterification of algal biomass. Maximum biodiesel recovery of 77.6 ± 2.3 wt.%

$$\underset{\textbf{FFAs}}{R_1-\overset{\overset{\displaystyle O}{\|}}{C}-O\text{-}H} \;+\; \underset{\textbf{Potassium Hydroxide}}{KOH} \;\rightarrow\; \underset{\textbf{Soap}}{R_1-\overset{\overset{\displaystyle O}{\|}}{C}-O-K^{+}} \;+\; \underset{\textbf{Water}}{H_2O}$$

Fig. 2. Formation of saponified product (soap).

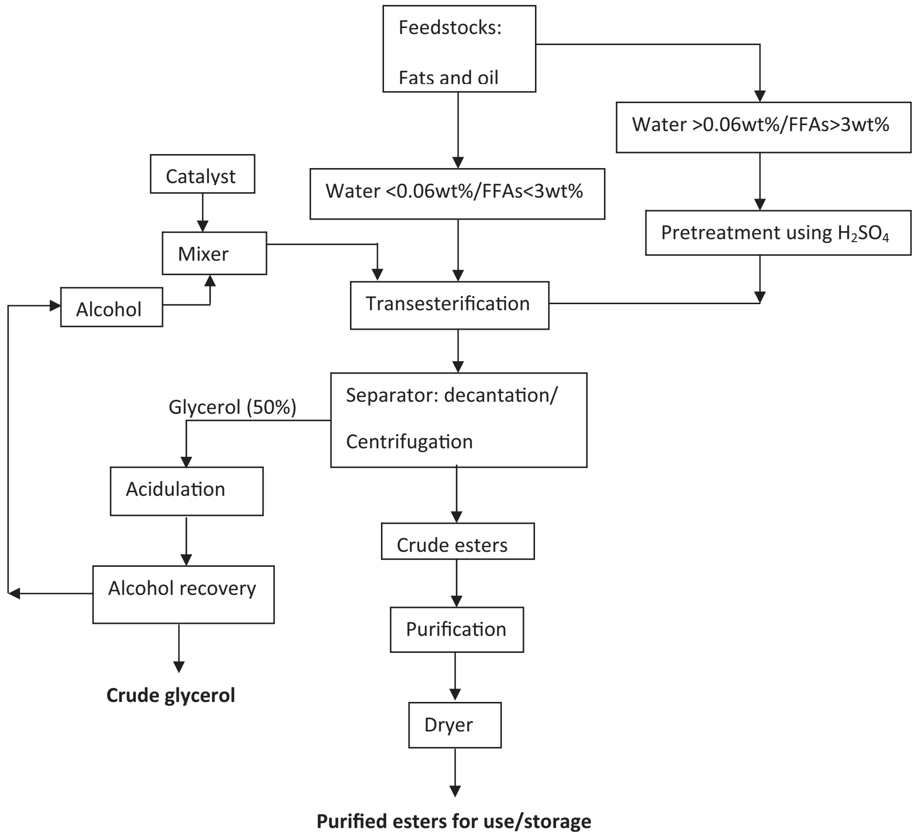


Fig. 3. Schematic diagram of alkali-catalyzed transesterification for alkyl esters production.

was achieved using a catalyst:lipid (NaOH) molar ratio of 0.15:1 and a methanol:lipid molar ratio of 600:1 and at a reaction time of 75 min. The authors performed additional runs at the optimum methanol to oil ratio of 600:1 in order to compare results achieved via alkaline catalyst with an acid catalyst. At lower reaction times, the alkaline catalyst (NaOH) provided high conversion than the acid catalyst (H_2SO_4). However for longer reaction times, acid catalyst ratio of 0.35:1 yielded higher conversions, up to 96.8 ± 6.3 wt.%, and may have facilitated the breakage of microalgae cell walls.

2.1.2. *Effects of water on acid-catalyzed transesterification reaction*

The most effective acid catalysts commonly used in the production of biodiesel include amongst others: sulfuric acid, hydrochloric acid and sulfonic acid. Sulfuric acid is mostly preferred as acid catalyst because of its low cost [27]. Besides sulfuric acid catalyst provide higher yield of esters but the reaction rates are slow [21]. Acid-catalyzed esterification reactions are also inhibited by presence of water. Thus, in designing methods to produce biodiesel using low quality feedstocks (soapstock), it is necessary to consider its high water content, amount of FFAs and acylglycerols [78]. Huang and Chang [77] reported that the water in the residual oil (spent bleaching earth) was reduced by evaporation at a temperature of 105 °C prior to esterification process. The authors noted that it would be difficult to reduce the FFAs content in oil to the desired level of 2% or less if water is not removed prior to the esterification process. Furthermore, Canakci [33] reported that during acid-catalyzed transesterification, conversion rate of soybean oil to methyl ester dropped from 90.54% to 58.77% when the FFAs level increased from 5% to 33%. The author noted that water content of feestocks should not exceed 0.5 wt.% to achieve more than 90% ester yield when using sulfuric acid as catalyst under the following operating conditions: temperature 60 °C, methanol-to-oil molar ratio 6:1, 3 wt.% sulfuric acid and 96 h. As well, Helwani et al. [76] remarked that acid-catalyzed transesterification is particularly sensitive to water concentration. The authors reported that water concentration is more critical in acid catalysis than in base catalysis. However, none addresses the cause for the observed difference in transesterification sensitivity to water using either base or acid catalysts. The authors also reported that presence of polar compounds could slow down transesterification reaction under acid-catalyzed conditions. Since water can form water-rich clusters around protons (solvent–proton complexes) with less acid strength than methanol-only proton complexes. In addition increase in water concentration might deactivate some of the catalyst. The less hydrophobic water-rich methanol proton complexes compared to methanol-only clusters could make it harder for the catalytic species (H^+) to approach the hydrophobic triglycerides (TG) molecules that eventually contributes to catalyst deactivation [76]. Also, water from feedstocks or produced during course of reaction may lead to deactivation of the catalyst by hydration [81]. As well increase in water concentration is established to have more effects on transesterification reaction than esterification reaction. This is due to the presence of polar carboxylic functional groups in FFAs that allows FFAs to interact readily with polar compounds, thus promoting alcoholysis reaction [76].

Otadi et al. [82] stated that since FFAs and water in the waste oil will reduce process efficiency, the concentration of these components should be reduced to a low value (<1% FFA) by means of esterification prior to transesterification process. Siddiquee and Rohani [83] reviewed biodiesel production using municipal sewage sludges. The authors noted that acid catalyzed transesterification reaction is slow. Besides, water produced during esterification of FFAs renders it much slower, hence acid-catalyzed esterification followed by base-catalyzed transesterification can be used

for the conversion of sewage sludge to biodiesel. Shuit et al. [84] remarked that J. curcas L. seeds are actually a very promising feedstock for biodiesel production using acid-catalyzed reactive extraction in comparison to municipal sludges, since these wastes could contain a lot of impurities such as water that might affect the reactive extraction process. Zheng et al. [85] have transesterified waste frying oil containing considerable amount of water and FFAs to biodiesel. At 70 °C with oil:methanol:acid molar ratios of 1:245:3.8, and at 80 °C with oil:methanol:acid molar ratios in the range 1:74:1.9–1:245:3.8, the transesterification was essentially a pseudo-first-order reaction as a result of the large excess of methanol which drove the reaction to completion (99.71% at 4 h). The authors noted addition of large excess methanol aided conversion of FFAs to methyl esters within the first few minutes under the prevailing reaction conditions.

2.2. Effects of water on enzymatic-catalyzed transesterification reaction

In enzymatic-catalyzed transesterification, presence of water has insignificant effects on the conversion of triglycerides to biodiesel products [21,86]. The activity of enzyme is easily affected by the water or solvent in the surrounding region [87]. In an essentially non-aqueous media, water plays several roles on the lipase-catalyzed transesterification reaction for the production of biodiesel and it has strong influence on the stability and catalytic activity of the lipase. Usually, some amount of water is required to sustain the activity of the enzyme in organic solvents. Conversely, water might play a part in the transesterification reaction, as a result influencing the equilibrium. Lipase possesses distinct feature of acting at the interface between an organic phase and an aqueous phase, thus the lipase activity is generally dependent on the interfacial area. Water helps in increasing the available interfacial area; hence it assists in maintaining lipase activity. On the other hand, lipase is rendered more flexible when excess water is used and this result to some unintended side-reactions such as hydrolysis, particularly in the transesterification process. Therefore the optimum water content required to maximize enzymatic activity is determined for most lipases, and the amount for a certain reaction is dependent on the nature of feedstock, the lipase, the immobilized support and the organic solvent used. In addition, high biodiesel yield could be obtained with commercial Novozym 435 lipase without necessarily adding extra water. Whilst the optimum amount of water required for Candida sp. 99–125 lipase to maintain the highest transesterification activity is 10–20% based on the oil weight [88]. According to Antczak et al. [89] water concentration in the reaction mixture (usually assayed by Karl-Fischer method and expressed as percentage content, %) is one of the most important factors that control lipase-catalyzed transesterification reaction rate and yield of biodiesel. The authors reported that the results of many studies on enzymatic synthesis of biodiesel show that in practice it is more convenient to present the yield of transesterification as a function of percentage water content in reaction system (%) since water is usually added to the system to increase catalytic efficiency of enzymes. Shah and Gupta [47] investigated the effect of water content on *Pseudomonas cepacia* lipase-catalyzed transesterification of Jatropha oil with ethanol for the production of biodiesel. The authors noted that biodiesel yield increased when water quantity ranging from 1% to 10% (w/w, enzyme) was added. They stated that at water content of 5%, the yield was 98 wt.% and when water was not added the yield was only 70 wt.%. Similarly, Lara Pizarro and Park [48] studied the effect of water on methanolysis. The water content of the mixture was varied from 15% to 100% (by weight of substrate). The methyl ester production increased with increased in the amount of water, but an abrupt decrease was noticed at water contents of 50% and 100%. The methyl ester conversion was highest (17.5%, w/w) after 24 h of reaction with water content of 75% (w/w). The authors stated that for extracted oils due to their greater viscosity, reaction carried out with 75% (w/w) water content was essential in speeding up the mixing of substrate and guaranteeing a greater oil-water interface area at which *Rhizopus oryzae* lipase displays higher activity [48]. Also, lipase-catalyzed transesterification can be applied on refined and raw plant oils, FFAs, waste fats from frying, tallow, etc., and to various alcohols such as methanol, ethanol, propanol, isopropanol, butanol, and isobutanol. But, low water concentrations in reaction medium can have a positive impact on productivity of biodiesel. Furthermore, soybean oil was transesterified using methanol and ethanol in the presence of *P. cepacia* lipase. Addition of initial water content of 0.01–2 g caused an increase in concentration of FFAs. Thus during ethanolysis a decreased in yields of esters was noticed when the water content was above the optimum (0.2–0.5 g), while addition of 0.01–2 g of water in methanolysis led to increase in FFAs concentration but did not decrease the yield of transesterification [89,90]. Similarly, Watanabe et al. [91] studied C. Antarctica lipase-catalyzed transesterification of waste plant oils in a solvent-free system. The water formed during production of methyl esters from fatty acids was bound by the secondary by-product, glycerol and a gradual increase in the concentration of methyl esters was observed. In another study, Chowdary and Prapulla [92] found that when water content in the reaction mixture was 0.96, hydrolysis of alkyl ester was fast and formation of butyl butyrate was slow. But when the water content in the reaction mixture was reduced to 0.33, the rate of transesterification was significantly improved. In addition, the effects of moisture content of various organic solvent used as a medium for *Candida cylindracea* lipase-catalyzed transesterification of (2*R**,3*S**) methyl *trans* 3-(4-methoxyphenyl) glycidate with aliphatic alcohols were investigated [93]. As well, Cernia et al. [94] have investigated in-depth influence of the reaction medium during transesterification reaction of (2*R**,3*S**) methyl *trans* 3-(4-methoxyphenyl) glycidate with aliphatic alcohols using a lipase from *P. cepacia*. The authors stated that use of hydrophobic solvents in lipases bio-catalyzed reactions could preserve enzyme conformational rigidity and stability. Du et al. [95] stated that the water contained in the immobilized lipase did not speed up the acyl migration during immobilized lipozyme TL-catalyzed three-step methanolysis for the production of biodiesel.

Moreover, the effect of water on enzymatic activity was studied by Iso et al. [96]. They added a little amount of water in the reaction mixture of 1-praponal and triolein as substrates and immobilized *Pseudomonas fluorescens* lipase as an enzyme. The authors observed that the conversion ratio was highest at 0.3 wt.% of water content, and the activity of the enzyme at 0.3 wt.% was about 17% higher than in the absence of water. They noted that enzymatic activity gradually decreased at more than 0.3 wt.% of water content. Li et al. [97] observed that water can influence biodiesel yield, but almost had no influence on the operational stability of the lipase. The authors noted that enzymatic-catalyzed transesterification can provide over 90% biodiesel yield. Further, at low water concentration, lipases can display high catalytic activity and high selectivity during transesterification reaction [98]. In another study, Masaru et al. [99] studied methanolysis of vegetable oil using lipases from *Candida rugosa*, *P. cepacia*, and pseudomonas fluorescens. The catalysts displayed high catalytic activity. The rates of methanolysis catalyzed by *C. rugosa* and *P. fluoresens* lipases decreased significantly when the water content was low, since water prevents the inactivation of these lipases by methanol. However the rate of methanolysis catalyzed by *P. cepacia* lipase remained high even under low water content, hence the rate of methanolysis catalyzed by *P. cepacia* lipase increased with decreased water content. Thus *P. cepacia* lipase is recommended for methanolysis process.

Wang et al. [100] used a packed-bed reactor system with lipase–Fe_3O_4 nanoparticle biocomposite catalyst for the continuous production of biodiesel. The increase in the conversion rate compared to batch process was possibly due to the decrease in the deactivation of the lipase–nanoparticle biocomposite resulting from the high methanol concentration and shearing force. The authors noted that emulsification of the reaction mixture had a beneficial effect on methanolysis through formation of oil–water droplets, thereby increasing the available interfacial area. In addition, because the lipase catalysis occurs in the interfacial layer between the hydrophobic and hydrophilic phases, the much larger surface area of the water/oil interface seems to result in an increased accessibility of the substrates to the lipase [100]. Furthermore, Chen et al. [101] reported that lipase as a form of protein, requires water presence to maintain its live tridimensional structure. They noted that water content affects the activity of the enzyme in non-aqueous media. The authors examined the reaction using water content ranging from 0% to 20% of the waste cooking oil (WCO) with 25% enzyme and 15% solvent of the WCO and 1.0 ml min^{-1} of reactant flow at temperature of 40 °C. The result showed biodiesel content increased steadily as water content increased from 0% to 10% of the WCO, and then declined as water content increased from 10% to 20%. The maximum biodiesel content was attained at water content of 10 wt.% which was about 138.4% higher than that in absence of water. They observed that excessive water content affected the mass transfer of the oil phase of the reaction product, and inhibited esterification. Salis et al. [102] noted that there are contradictory reports on the effects of water content in the transesterification of triglycerides to biodiesel. They stated that some authors were of the opinion that presence of high amounts of water in the system could increase the yield of biodiesel, while others emphasize the contrary. This clear contradiction might be clarified by considering that the effect of water in these systems depends on the enzyme, the support and the medium (solvent or solvent-free). Therefore, as a general consideration, high water content should decrease ester yield since undesirable triglyceride hydrolysis occurs [102].

2.2.1. Effects of water on solid-catalyzed transesterification reaction

The need to develop heterogeneous catalysts such as solid catalysts for the production of biodiesel is increasingly becoming important due to the problems associated with homogeneous catalysts. Li et al. [87] reported that synthesis of biodiesel via solid catalysts has been its advantages of efficient separation, free of corrosion and environmental friendliness. The authors used solid superacid catalyst ($SO^{-2}{}_4/ZrO_2$–TiO_2/La^{3+}) as an effective catalyst for the simultaneous transesterification and esterification. At optimized reaction conditions: molar ratio of alcohol/oil of 15:1, catalyst amount of 5 wt.%, temperature of 200 °C reaction time of 2 h, biodiesel yield above 90% could be obtained. Boey et al. [103] remarked that among the heterogeneous catalysts, CaO shows potential in the transesterification reaction. The catalyst has tolerance to moisture and FFAs, is reused, is inexpensive, has low methanol solubility, is non-corrosive and is environmental friendly. Similarly, Zabeti et al. [61] noted that presence of little amount of water in reaction system can enhance the catalytic activity of calcium oxide (CaO) and increase biodiesel yield. This is because presence of water, O^{2-} on the surface of the catalyst extracts H^+ from water molecules to form OH^- which subsequently extracts H^+ of methanol to form methoxide anions, which are the real catalysts for transesterification reaction. The authors stated that when 2.03 wt.% water was added into the reaction medium of 12:1 alcohol/oil molar ratio and 8 wt.% catalysts, the methyl ester yield exceeded 95% within 3 h of reaction time compared to 80% under anhydrous conditions. They reported that no leaching of the active site of catalyst was observed into the reaction media and the activity of the catalyst was stable after 20 cycles of the reaction [61]. Additionally, Chew and Bhatia [67] reported high activity of the solid acid catalyst used. The catalyst provided high yield (99%) of biodiesel using low catalyst concentration (1.85×10^{-3}:1 weight ratio of catalyst to-oil), low methanol-to-oil ratio (5.3:1) in a relatively short reaction time (45 min) at low temperature (338 K). The authors noted that the activity of the Cs2.5PW was not considerably affected by the moisture content, and the catalyst was easily separated from the product mixture and reused a number of times. In another study, Abreu et al. [104] used tin oxide (Sn(3-hydroxy-2-methyl-4-pyrone)2$(H_2O)_2$) to transesterified soybean oil to biodiesel. The catalyst was anchored by BMI(PF6) and DOWEX acid resin respectively. In case of the former, two-phase system was obtained by mixing the solution of the tin complex in ionic liquid, methanol and soybean oil, which was kept in reflux for 1 h. Then, water was added to the reaction mixture and a three-phase system was obtained with upper layer containing the fatty acid methyl esters, the middle one composing of water and hydroxyl compounds, and the bottom layer containing the ionic liquid, all of which were separated by simple decantation. The authors noted that it was not possible to obtain a recyclable multi-phase system anchoring the tin complex to an ionic liquid or to a solid phase. The tin oxide catalyst provided high conversion yield of up to 93% in 3 h. They reported absence of emulsion at the end of the reaction. The activity of the catalyst was completely preserved after using it three more times, under the same reaction conditions. Endalew et al. [105] noted that solid acid catalysts can catalyze both esterification and transesterification simultaneously and are insensitive to FFAs and water. They stated that the catalysts are comparatively cheaper and can be effectively used in continuous fixed bed reactors. Jacobson et al. [64] explored different types of solid acid catalysts such as MoO_3/SiO_2, MoO_3/ZrO_2, WO_3/SiO_2, WO_3/SiO_2–Al_2O_3, zinc stearate supported on silica, zinc ethanoate supported on silica and TPA supported on zirconia for the simultaneous catalysis of esterification and transesterification reaction of waste cooking oil to biodiesel. The authors noted that solid acid catalysts having interconnected system of large pores, moderate to strong acid sites and hydrophobic surface could be ideal for biodiesel preparation. They reported that the catalytic activities of the catalysts were not affected, with Zi/Si catalyst providing maximum ester yield of 98 wt.%.

In addition Ramos et al. [106] examined the catalytic performance of three catalysts; zeolites mordenite, beta and zeolite X. The high catalytic activity of NaX catalyst at low temperatures during transesterification makes it more advantageous than the homogeneous catalyst. However, the catalyst active sites were leached out to the product during the course of the reaction. Thus efforts have to be made to ensure long term stability of the catalyst. Further, Olutoye and Hameed [107] synthesized biodiesel from used cooking oil by means of solid reusable $Mg_{1-x}\,Z_{n1+x}O_2$ catalyst. The authors noted that used oil contains a high amount of water which may lead to hydrolysis of esters and triglycerides during transesterification reaction. Hydrolysis is an undesirable side reaction that could lower yield of esters and add more to the cost of production. Highest ester content of 80%, was achieved with the catalyst during 4 h 15 min reaction time at 188 °C with methanol to oil ratio of 9:1 and catalyst loading of 2.55 wt.% oil. Melero et al. [108] produced biodiesel from crude palm oil containing high percentage of FFAs over sulfonic acid-functionalized SBA-15 materials (propyl-SO_3H, arene-SO_3H, perfluoro-SO_3H). The high catalytic activity achieved over these modified materials was attributed to increased hydrophobicity near the sulfonic acid moieties and enhanced diffusion of reactant and products within the hydrophobic mesopores. In addition, functionalization of arene-SO_3H (SBA-15) catalyst with hydrophobic trimethylsilyl groups improved its catalytic

performance. The catalyst gave biodiesel yield of 95 wt.% as determined by ^{1}H NMR in 4 h of reaction with a moderate methanol to oil molar ratio (20:1), 140 °C and a catalyst concentration of 6 wt.%. Gao et al. [109] prepared solid base catalyst KF/Ca–Al hydrotalcite from Ca–Al layered double hydroxides. The catalyst was successfully used in the transesterification of palm oil with methanol to produce biodiesel. The activity of Ca–Al mixed-oxides had been significantly improved with loading of KF. At optimal condition: 338 K, catalyst amount 5% (wt./wt. oil) and methanol/oil molar ratio 12:1, and 3 h reaction time, for the mass ratio 100 wt.% (KF·6H_2O to Ca–Al mixed-oxides), the yield of esters could reach 97.98%. Further the active site of catalyst was maintained without leaching being noticed.

Besides, Sankaranarayanan et al. [110] have transesterified used cooking oils, non-edible and edible for the production biodiesel using calcined layered double hydroxides as reusable base catalysts. The activity of the catalyst was determined in the presence of different concentrations (0–20%) of oleic acid (as a model FFA)/water separately). The yield of esters gradually decreased when the concentration of the impurity such as water increased under optimized conditions. Thus modifications of reaction conditions are required to achieve high yields of esters when working with different grades of methanol that have varied water content and different oils. Yan et al. [111] examined the effects of water and FFAs on the activity of Ca_3La_1 using food-grade soybean oils with 1.0%, 2.0%, 4.0% and 10.0% of water, and with 0.5%, 1.1%, 1.6%, 3.6%, 5.1% and 7.0% of FFAs. Addition of water slightly decreased the reaction rate and prolonged the time to get to highest yield of esters. When water was not added biodiesel yield of 94.3% was achieved within 60 min, but when water was added the time to reach 94.8% biodiesel yield increased to 90 min. The authors noted that for Ca_3La_1-catalyzed transesterification, addition of water had nearly no negative effect on the yield of esters. Conversely, increased in water for both NaOH or H_2SO_4-catalyzed transesterification led to gradual decrease in esters yield. When 4.0% of water was added to NaOH and H_2SO_4-catalyzed transesterification, ester yield decreased to 79.0% and 21.2% respectively, but ester yield for Ca_3La_1 was maintained at 94.8%. The result indicated that Ca_3La_1 could remarkably tolerate water in the transesterification reaction compared to NaOH and H_2SO_4. This can be attributed to the fact that H_2O does not change the total basicity of the Ca_3La. Jin et al. [112] developed $ZnO/La_2O_2CO_3$ layered composite heterogeneous catalyst for the efficient ultra-fast microwave biofuel production. Under mild reaction conditions, the yield of esters was above 95% with less than 1.0 wt.% catalyst. The authors remarked that determination of the amount of the catalyst leached is very important for the following reasons: leached metal ions can form unwanted soap and water byproducts, presence of the catalyst in the alcoholic phase and in the ester phase have implications in water consumption for rinsing of the products, creating environmental issues, and increasing the biodiesel cost, and runs are affected by the degree of leaching when working in a continuous process. The authors remarked that the catalytic performance $ZnO/La_2O_2CO_3$ was maintained after storing the catalyst in air for a month and no catalyst leaching into the products was found based on XRF analysis. Also, Morale et al. [113] evaluated different lipidic wastes and low-grade oils and fats as feedstocks for the acid-catalyzed biodiesel production. Arene sulfonic acid-functionalized SBA-15 silica catalyst has provided yield of esters close to 80% in the simultaneous esterification–transesterification of the different feedstocks, regardless of their nature and properties, using methanol under the following reaction conditions: 160 °C, 2 h, methanol to oil molar ratio of 30, 8 wt.% catalyst loading, and 2000 rpm stirring rate. Further low-grade oils and fats contain a number of impurities such as unsaponifiable matter, water, phosphorous and metals, having a negative effect on the yield of esters, thereby compromising the reutilization of arene sulfonic acid-functionalized SBA-15 catalyst.

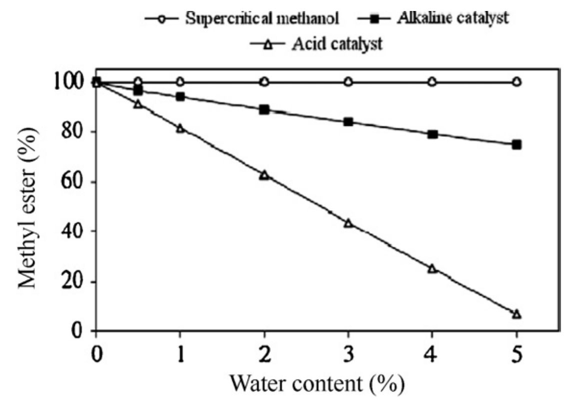


Fig. 4. Yields of methyl esters as a function of water content in transesterification of triglycerides.

2.3. *Effect of water on non-catalytic transesterification reaction*

In supercritical methanol method, presence of water positively affects the formation of methyl esters [114]. Water promotes the mechanisms of non-catalytic supercritical reaction [76]. Kusdiana and Saka [36] studied the effect of water on esters yield in the methyl esterification of fatty acids and transesterification of triglycerides prepared by catalyst-free supercritical methanol. Rapeseed oil mixed with methanol containing 10%, 18%, 25% and 36% water were subjected to supercritical treatment. At the end of the reaction performed at a temperature of 350 °C, pressure of 43 MPa, molar of 42:1, and 4 min reaction time; the mixtures were all completely converted to methyl esters. The authors stated that in supercritical methanol method, water presumably acts as an acid catalyst more strongly than methanol itself [36]. However, water does not have a significant effect on the biodiesel yield, as complete conversions could always be achieved regardless of the content of water [115] as shown in Fig. 4 [36]. In another study, Saka and Kusdiana [116] stated that increase in yield in supercritical process could be due to the conversion of FFAs to methyl esters. The authors noted that, FFAs which are converted in the conventional method to soaps formation by the alkaline catalyst were found to be converted to methyl esters through the dehydration reaction during the supercritical treatment of methanol. This process is reported to provide high-quality biodiesel [117]. Table 3 demonstrates higher yields of biodiesel when supercritical process is used [116]. Furthermore, in the catalytic supercritical methanol method, the conversion of triglycerides to biodiesel rises from 60% to 90% for the first 1 min and 50–95% for the first 8 min respectively [118]. Moreover Tan et al. [119] investigated prospects of non-catalytic supercritical methyl acetate process for biodiesel production. They revealed that supercritical methyl acetate (SCMA) could achieve 99 wt.% when the operating conditions are fixed at 400 °C/and 220 bar for reaction

Table 3
Comparison between the common method and the supercritical methanol method for biodiesel production [116].

	Common method	SC MeOH method
Reaction time	1–8 h	120–240 s
Reaction conditions	0.1 MPa, 30–658 °C	>8.09 MPa, >239.48 °C
Catalyst	Acid or alkali	None
Free fatty acids	Saponified products	Methyl esters
Yield	Normal	Higher
Removal for purification	Methanol, catalyst and saponified products	Methanol
Process	Complicated	Simple

temperature, methyl acetate/oil molar ratio of 30:1 and 60 min of reaction time. They reported that, SCMA did not suffer from adverse effect with the presence of impurities such as water and FFAs, proving that SCMA has a high tolerance toward contamination which is crucial to allow the utilization of inexpensive waste oils and fats as biodiesel feedstock. In fact the yields increase steadily in SCMA and supercritical methanol (SCM) reactions with the increment of water content until 20% to produce yields of 108 wt.% and 87 wt.%, respectively.

Sawangkeaw et al. [120] stated that supercritical methanol process is suitable for the conversion of spent oils or other low-grade feedstocks to esters at 270–300 °C, pressure of 20–35 MPa, methanol to oil molar ratio of 24:1–42:1 and a longer reaction time than the conversion of lipid at 400–450 °C which employs 10–20 MPa and 6:1–9:1 methanol to oil molar ratio to yield a nearly complete reaction. Although, a high temperature clearly enhances the rate of reaction, an excessively high temperature can lead to a negative effect on the esters content. But thermal degradation of unsaturated fatty acids (UFA) can occur at temperature range of 320–350 °C. Demirbas [121] transesterified waste cooking oil via supercritical methanol in a 100-ml cylindrical autoclave at temperatures of 520, 540, and 560 K, and molar ratio of methanol to waste cooking oil: 41:1. The sample was charged through the bolt-hole into the autoclave, and the hole was plugged with a screw bolt after each run. In each run, the autoclave was charged with a certain amount of waste cooking oil (20–30 g) and methanol (5–50 g). The autoclave was heated using an external heater, and the power was adjusted to give an approximate heating time of 30 min. The reaction temperature of the vessel was measured with an iron-constantan thermocouple and controlled at $\pm$5 K for 30 min. Further supercritical transesterification can yield high-purity methyl esters (99.6%) and pure glycerol (96.5%). The authors stated that owing to high cost of the fresh vegetable oil, waste cooking oil might be available with relatively cheap price for biodiesel production. Also, since waste cooking oil contains large amount of water and free fatty acids, supercritical transesterification of such oils could offer great advantages such as elimination of pre-treatment and operating costs that are common with conventional biodiesel production process [121]. Similarly, Manuale et al. [122] investigated conversion of waste oils to biodiesel in supercritical methanol using the following conditions: methanol-to-oil molar ratios of 15 and 20, temperature of 280 °C. The formation of water was attributed to esterification of free fatty acids and glycerol decomposition. They concluded that in the reaction conditions of the non-catalytic supercritical transesterification of glycerides, the glycerol can react forming water and volatile products, possibly carbon dioxide. This water can react with triglycerides forming FFAs. Water can also react with glycerol generating volatile products such as carbon dioxide and hydrogen. The authors reported that the yield of the process is 103% and the consumption of methanol was higher than the theoretical value. This indicated that some methanol is probably inserted into middle positions of the acyl chain. Patil et al. [123] studied a one-step process for direct liquefaction and conversion of wet algal biomass containing about 90% of water to biodiesel under supercritical methanol conditions. This one-step process enables simultaneous extraction and transesterification of wet algal biomass. The process conditions are milder than those required for pyrolysis and prevent the formation of by-products. In the proposed process, esters can be produced from polar phospholipids, free fatty acids, and triglycerides.

3. Raw materials for biodiesel production

Animal fats and vegetable oils are the main raw materials usually employed to produce biodiesel. Also, oils from algae have shown some promise as raw materials for biodiesel production. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdoms that are made up of one molecule of glycerol and three molecules of fatty acids and are commonly referred to as triglycerides [124]. Chemically, oils and fats consist of 90–98% triglycerides and small amount of mono and diglycerides [14]. Vegetable oils and their derivatives are attractive as alternative fuels, fuel extenders, and additives in diesel engines; this is because they can improve engine performance. Various biofuels derived from fats and oils have been widely tested as alternative fuels [30]. Methyl esters from fats and oils generally referred to as 'biodiesel," are prominent candidates as alternative diesel fuels [38]. Canoir et al. [125] reported that transesterification of triglycerides for biodiesel production has been extensively studied in recent years. The raw materials being exploited commercially by the biodiesel countries constitute the edible oils derived from rapeseed, soybean, palm, sunflower, coconut, and linseed [126]. Additionally, majority of research activities currently going on are focused on selectively breeding or genetically engineering varieties of oil seeds to produce an optimal blend of fatty acids for biofuel production [127]. Cardone et al. [128] studied use of *Brassica carinata* oil for biodiesel production. *B. carinata*, a native plant of the Ethiopian highlands widely used as food by the Ethiopians, has recently become a subject of increasing interest. The authors noted that the crop is being experimented due to its better agronomic performances in areas such as Spain, California and Italy that are characterized by adverse environmental conditions for the cultivation of *Brassica napus*. Also, Geller et al. [129] stated that unprocessed, commercial vegetable oils (soybean, canola, etc.) can be effectively used by diesel engines. The authors noted that long-term use of unmodified vegetable oils in compression ignition (diesel) engines might lead to build-up of carbon deposits on the fuel injectors due to incomplete combustion of these fuels. The authors investigated the potential of genetically modified plant strain (*Cuphea viscosissima* VS-320) oil with medium- and short-chain triglycerides as sources of fuels for diesel engine consumption. They noted that these oils may possibly avoid cost of both transesterification and refining of crude biodiesel products, since they possess characteristics similar to diesel fuels. In addition, Antolın et al. [19] stated that biodiesel obtained from energy crops could generate favorable effects on the environment, such as decreased acid rain and reduced greenhouse gas effect caused by combustion.

3.1. Raw materials containing less water content

As earlier mentioned refined raw materials are preferred during transesterification of triglycerides to fatty acid alkyl esters, especially when alkaline catalyst is used. Refined raw materials consist of little amount of impurities such as water, and FFAs contents. The used of refined raw materials could yield high-purity and quality biodiesel with physicochemical properties comparable to diesel fuels. Demirbas [130] stated that the major economic factor to be considered as input costs for biodiesel production is the cost of feedstocks. Similarly, Dube et al. [131] noted that the most significant factor in the financial assessment of esters production process is the high cost of refined/virgin oils. Van Gerpen [132] observed that refined raw materials could provide methyl ester yield ranging from 93% to 98% compared to crude raw materials providing methyl esters yield ranging from 67% to 86% for crude oil. As well, the yield of biodiesel from refined vegetable oils was reported to be close to 99% [89].

3.2. Raw materials containing large amount of water

Kusdiana and Saka [36] reported that high water and FFAs contents of waste vegetable oils and crude oils may hinder their effective conversion to biodiesel fuel. Canakci [33] noted that waste cooking oils, restaurant grease and animal fats are potential raw materials for biodiesel production. The levels of moisture of these feedstocks vary from 0.01 to 55.38 wt.%. This wide range shows that the method required to convert waste grease and animal fats to biodiesel must tolerate a various range of raw materials properties. The author noted that biodiesel production from low quality raw materials is expected to benefit from their lower cost and this will help to reduce overall cost of production. Table 4 presents chemical analysis of restaurant grease and animal fat samples [33]. Jaruwat et al. [133] noted that biodiesel production is sensitive to the FFAs (>0.5%, w/w) and water contents of the oil and these two components are much in waste oils and fats. Similarly, Ramadhas et al. [134] stated that low quality raw materials could not be transesterified using the commercially available alkali-catalyzed transesterification process. In another study, Haas [78] remarked that as opposed to virgin fats and oils and recycled greases; soapstock contains much water content which is heavily emulsified with the lipid constituents and it is difficult to remove. According to Ikwuagwu et al. [135] moderately high moisture content may cause a serious degradation of the fatty materials through hydrolysis, and also lower its material stability. As well, Khan and el Dessouky [136] noted that vegetable oil used for the production of biodiesel must be substantially anhydrous otherwise the process could be very challenging. The authors reported that the moisture content of the oil is recommended to be removed using silica gel.

3.3. Effects of water content of microalgal oil as raw materials

Microalgae are classified into four categories: diatoms, green algae, blue-green algae and golden algae. Microalgae are microscopic photosynthetic organisms that are found in both marine and freshwater environments [137]. Oleaginous microorganisms like microalgae, bacillus, fungi and yeast are all available for biodiesel production [138]. Microalgae have been recommended as good sources for fuel production because of their advantages of superior photosynthetic efficiency, higher biomass production and faster growth rates compared to other energy crops [139]. Khan et al. [140] noted that microalgae are photosynthetic microorganisms which convert sunlight, water and CO_2 to sugars, from which macromolecules, such as lipids and triacylglycerols (TAGs) can be obtained. These TAGs are promising and sustainable feedstocks for biodiesel production. The authors stated that microalgal biorefinery approach can be used to reduce the cost of making microalgal biodiesel. Also, microalgal-based carbon sequestration technologies can cover the cost of carbon capture and sequestration [140]. Similarly, Mata et al. [141] noted that microalgae as feedstock for the production of biofuel potentially offer great opportunities in the longer term. In another study, Chisti [142] stated that microalgae emerge to be the only biodiesel source that is possibly capable of completely displacing petro-diesel as shown in Table 5 [141]. Unlike other oil crops, microalgae can grow rapidly and are extremely rich in oil. The authors noted that microalgae could double their biomass within 24 h, as well microalgae can grow practically in every place where there is enough sunshine. Some microalgae can grow in saline water. The most significant difference of algal oil is in the yield and its biodiesel yield [130]. It was also remarked by Demirbas [143] that algae will one day be competitive source for biofuel production. The author noted that the moisture content of microalgal oil was determined by drying a 3–5 g sample at 378 K to constant weight, which was carried out at 1025 K for 2 h. According to Huang et al. [144], microalgae contain high

Table 4
Chemical analysis results of restaurant grease and animal fat samples [33].

Test/sample	Soy oil 1	Soy oil 2	SIM-01	SIM-02	SIM-03	SIM-04	SIM-05	SIM-07	SIM-08	SIM-09	SIM-10	SIM-11	SIM-24
MIU (%)	0.44	0.41	24.11	0.74	2.85	3.54	0.98	6.42	58.14	1.71	1.06	1.97	2.37
Moisture and volatiles by hot plate	0.01	<0.10	18.06	0.31	0.11	3.11	0.35	0.26	55.38	1.26	0.65	1.42	0.35
Insoluble impurities (%)	<0.10	<0.10	1.22	<0.10	0.11	0.09	0.11	3.83	2.51	0.03	0.03	0.08	1.03
Unsaponifiable matter (%)	0.43	0.41	4.83	0.43	2.63	0.34	0.52	2.33	0.25	0.42	0.38	0.47	0.99
Peroxide value (mequiv./kg)	66	7.3	0.8	4.0	<0.2	3.7	3.4	<0.2	0.6	4.6	3.1	1.7	1.0
FFA (%)	0.02	0.01	41.8	9.7	25.7	2.6	1.1	25.5	14.8	0.7	1.3	0.7	10.5

SIM-01: unprocessed restaurant grease. As delivered. Collected from the tops of three separate barrels. Water mostly at the bottom of the barrel.
SIM-02: restaurant grease. Boiled and settled. This is the final product before mixing with animal fat.
SIM-03: animal fat. This was the final product for animal fat but before it is mixed with any restaurant grease.
SIM-04: processed restaurant grease.
SIM-05: restaurant grease. Skimmed from top of barrel.
SIM-07: mixed fat from storage tank. This is the rendered product as sold.
SIM-08: restaurant grease, partially processed. This material had been through the first stage of processing, where the solids and free water are removed but it had not been cooked.
SIM-09–SIM-11: restaurant grease. Skimmed from top of barrel.
SIM-24: finished grease, with some restaurant grease.

Table 5
Comparison of some sources of biodiesel [141].

Crop	Oil yield (l/ha)	Land area needed (Mha)[a]	Percent of existing US cropping area[a]
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Jatropha	1892	140	77
Coconut	2689	99	54
Oil palm	5950	45	24
Microalgae[b]	136,900	2	1.1
Microalgae[c]	58,700	4.5	2.5

[a] For meeting 50% of all transport fuel needs of the United States.
[b] 70% oil (by wt) in biomass.
[c] 30% oil (by wt) in biomass.

water content after harvest which requires a great deal of energy to remove the moisture from the algal cells during the period of pretreatment. The authors noted that high cost of oleaginous materials is the main problem hindering commercial production of biodiesel. Therefore, finding cheaper oleaginous materials and improving transesterification technologies are the key issues to the successful biodiesel production [144]. Zen et al. [145] noted that microalgal culture dewatering is a major obstruction to industrial-scale processing of microalgae for biofuels and other high-value biochemicals production due to the very dilute nature of harvested microalgal cultures, resulting in high energy consumption required for dewatering. Thus, Harun et al. [146] remarked that an optimum dewatering technique should be applicable to a wide range of microalgal strains, have high biomass recovery and also cost effective. It is therefore important to understand various technologies in cultivating and dewatering microalgae in order to maximize the production of microalgae at low cost.

4. Effects of water on refining of crude biodiesel

Refining of crude biodiesel consist of separation and purification processes. Separation and purification of transesterified products are usually required to achieve high-purity and quality biodiesel fuel that can be suitably used in diesel engines without necessary engine modifications. In conventional biodiesel production, separation and purification processes are rendered difficult if lower quality feedstocks containing high amount of water and FFAs are used. Water leads to the formation of emulsion, thereby limiting the tendency for the mixture to settle and get separated. Besides, formation of emulsion causes considerable loss of biodiesel yield [132]. Vicente et al. [147] stated use of refined sunflower oil containing less amount of water to produce biodiesel. The authors reported that after separation and purification stages, biodiesel yield was higher than 98 wt.% for the methoxide catalyst; this was because of the fact that the yield loss due to soaps formation and methyl ester dissolution in glycerol were negligible.

4.1. Effects of water on the separation of crude biodiesel

Antczak et al. [89] noted that chemical processes for biodiesel production are energy-consuming and produces undesirable by-products such as soaps and polymeric pigments that hinder separation of pure methyl or ethyl esters from glycerol and di- and monoacylglycerols. The separation of biodiesel from transesterified product mixture is an important step during biodiesel production. In many conventional processes, separation is carried out simultaneously with a purification process. This process includes centrifugation, standing separation and repeated water washing steps [38]. The water-added supercritical methanol method provides easier product separation, since glycerol, a by-product of transesterification, is more soluble in water than in methanol [146]. Van Gerpen [132] reported that water may be added to the reaction mixture after transesterification is completed to improve the separation of glycerol. According to Balat and Balat [148] gravity separation is suitable to recover biodiesel from by-product, glycerol. Demirbas [21] noted that water can cause soaps formation and frothing. The soaps formation can induce formation of gels and foams, increase in viscosity, and render separation of the by-product, glycerol very difficult [21,76,134,149,150].

The recent introduction of membrane technology in the refining of crude biodiesel has shown some promise in the removal of biodiesel impurities such as glycerol. Saleh et al. [151] employed membrane separation process to remove free glycerol from biodiesel. The separation of glycerol from crude biodiesel in the presence of water was determined by adding 0.06, 0.1 and 0.2 wt.% water to vacuum-treated fatty acid methyl esters. The results of the tests showed that addition of water in small amounts (0.06 wt.%), improved the separation process. The complete miscibility of glycerol and water caused the formation of larger particles and thus, two immiscible phases were formed: a water and glycerol phase, and a biodiesel phase. This suggested that the principle of separation of free glycerol from biodiesel is that of the retention of a finely dispersed water and glycerol phase by the membrane. The authors noted 80% of total amount of water used in conventional biodiesel purification to be saved. In the same way, Gomes et al. [152] investigated efficiency of microfiltration with ceramic membranes for the separation of biodiesel and glycerol. The excess ethanol used in the reaction varied from 60% to 100%. The mixtures with mass composition of 70% biodiesel, 10% glycerol, and 20% ethanol and 85% biodiesel, 10% glycerol, and 5% ethanol were prepared. The experiments were carried out with tubular Al_2O_3/TiO_2 ceramic membranes with average pore size of 0.2, 0.4, and 0.8 μm and filtration area of 0.005 m^2. The best glycerol retention of 99.6% was obtained through membrane with pore size 0.2 μm at a temperature of 60 °C and transmembrane pressure of 2.0 bars. In another study, Wang et al. [153] developed a ceramic membrane separation process for the refining of crude biodiesel in order to reduce considerable amount of water needed in the conventional water washing process. The authors noted that biodiesel concentrate should be carefully treated to improve the yield of the final product 0.02 wt.% (ASTMD6751).

4.2. Effects of water on the purification of crude biodiesel

Purification of crude biodiesel is required to remove contaminants such as free residual catalyst, soap, and excess alcohol, and make the fuel suitable for diesel engine consumption [154]. Balat and Balat [148] reported that after glycerol and biodiesel phases are separated, the excess alcohol in each phase is removed via flash evaporation process or by distillation. The authors stated that care must be taken to ensure that no water accumulates in the recovered alcohol stream. Karaosmanoğlu et al. [155] stated that to get pure biodiesel conformable to the international standard specifications, refining techniques such as washing with hot distilled water, petroleum ether and then washing with distilled water, and neutralization with H_2SO_4 (1:1) were experimented. Among these techniques, washing with hot distilled water at 50 °C was chosen as the best refining option. The purity of the biodiesel obtained was almost 99% [155]. According Agarwal et al. [156], the separated biodiesel from glycerol was mixed with warm water (around 10% volume of ester) to remove the catalyst and then the mixture was allowed to settle under gravity for another 24 h. The catalyst was dissolved in water and separated. The authors removed moisture from the purified biodiesel using silica gel crystals. In another study, Demirbas [157] reported addition of 28% of water by volume of oil to wash crude esters. The process was repeated until the ester layer became clear. The use of water to purify crude biodiesel

usually affects the yield of biodiesel [133]. Furthermore, Kaya et al. [158] stated that the crude methyl ester was purified by distilling off the residual methanol under normal atmospheric pressure, centrifugation, washing several times with water, and drying with vacuum desiccators to avoid deterioration of the final ester product. Mendow et al. [159] reported that after the biodiesel phase was separated from the glycerin phase, it was purified by washing first with acidified water, and then with water. They stated that these two washing steps are enough to remove all the phosphorus (P) left in the biodiesel phase. In one of the experiment, a very small amount of P (1.66 ppm) was found in the final biodiesel. Nevertheless, this is a negligible concentration, which is well below the maximum limit established in the EN 14214.

Additionally, Jain and Sharma [160] noted that biodiesel was separated, washed with water, dried over anhydrous sodium sulfate. The authors remarked that the final biodiesel fuel and can be used directly as fuel in diesel engines. de Jesus et al. [161] reported removal of residual catalyst by means of successive water washings. However use of water in the purification of crude biodiesel could result to wastewater discharges. Similarly, Janaun and Ellis [162] observed that water washing process consumes a lot of water to remove homogeneous catalysts and salt produced during biodiesel production. Besides, soap renders water washing process difficult, as a result the process requires large amount of water to eliminate all the impurities in biodiesel [36]. Alba-Rubio et al. [163] reported a new and effective procedure for rinsing the biodiesel by boiling it with a Na_2CO_3–methanol mixture followed by a final water rinsing step. The solid Na_2CO_3 can be easily removed by filtration. The Ca^{2+} and Na^+ contents were below 5 ppm in the final biodiesel sample, meeting the limits regulated by EN 14214. According to this procedure, biodiesel can be synthesized by incorporating Na_2CO_3 into the initial CaO–oil–methanol reaction mixture. After the filtration of the CaO catalyst and Na_2CO_3 cleaning agent as well as an additional water washing step, the Na^+ and Ca^{2+} contents in the final product were also below the levels required by the EN 14214 regulation.

Jaruwat et al. [133] remarked that the requirement of huge amount of water leads to considerable wastewater being generated. The authors stated that wastewater from biodiesel typically consists of pH: 9.25–10.76, COD: 312,000–588,800 mg/l, BOD: 168,000–300,000 mg/l, Oil and grease: 18,000–22,000 mg/l and total Kjeldahl nitrogen: 439–464 mg/l. The high values of these components potentially inhibit the growth of micro-organisms capable of naturally degrading the wastewater [133]. Therefore to circumvent these problems, some researchers claimed that it is possible to react the oil and methanol without a catalyst, so as to eliminate the need for the water washing step that is associated with wastewater discharges [116,164]. Saka and Kusdiana [116] reported that removal of catalyst and soap after transesterification reaction is essential. The authors found that supercritical methanol process leads to much simpler purification procedure because of the absence of catalyst. Furthermore, Saleh et al. [165] studied the effect of soap, methanol, and water on the glycerol particle size for the refining of biodiesel using membrane purification process. Addition of water played a significant effect in removing glycerol using membrane technology. As mentioned earlier, the water added increased the molecular size of glycerol and facilitated its retention. As a result, biodiesel with glycerol content of 0.013 wt.% was obtained. This value (0.013 wt.%) is below the value (0.020 wt.%) stipulated by ASTM D6751 and EN 14214 standards. The authors remarked the negative impact of methanol, and to a lesser extent of soap. They stated that to achieve ASTM standard specification for biodiesel, it is important for economic reasons to minimize the amount of methanol and soap, and evade water washing step so as to reduce environmental impact [166].

5. Effects of water on the quality of biodiesel fuel

The purity level of the esters has strong effects on its fuel properties [152]. The quality of biodiesel fuel is significant for its successful use on diesel engines and its subsequent replacement of non-renewable fossil fuels [166]. Meng et al. [138] stated that to assess the potential of biodiesel as a substitute for petro-diesel fuel, the properties of biodiesel such as density, viscosity, flash point, cold filter plugging point, solidifying point and heating value have to be determined. Additionally, the water content must be less than 0.1% (wt) and the acid value must be less than 1. According to ASTM 6751-3 and EN 14214 international standard specifications for alternative diesel fuels, the water, FFAs, methanol, and glycerol contents of the biodiesel must be of a minimum value and the fuel must be at least 96.5% pure [155] as presented in Table 6 [167]. DeMello et al. [168] stated that at pH values of 7.4 and 8.3, biodiesels have estimated base-catalyzed hydrolysis half-lives of 3 years and 19 weeks, respectively (25 °C). The authors observed that the rates of hydrolysis are slower than the microbial degradation rates of biodiesels, and that abiotic hydrolysis could become more relevant in conditions where microbial degradation is less ideal. It was observed by Burton [169] that biodiesel can absorb

Table 6
Biodiesel, B100, specification-ASTM D6751-06 [135].

Property	ASTM	Method limits	Units
Flash point	D93	130 min.	°C
Water and sediment	D2709	0.050	max. vol.%
Kinematic viscosity, 40 °C	D445	1.9–6.0	mm^2/s
Sulfated ash	D874	0.020 max.	mass%
Sulfur	D5453	–	–
S 15 grade	–	15 max.	ppm
S 500 grade	–	500 max.	–
Copper strip corrosion	D130	No. 3 max.	–
Cetane	D613	47 min.	–
Cloud point	D2500	Report	°C
Carbon residue 100% sample	D4530[a]	0.050 max.	mass%
Acid number	D664	0.50 max.	mg KOH/gm
Free glycerin	D6584	0.020 max.	mass%
Total glycerin	D6584	0.240 max.	mass%
Phosphorus content	D4951	0.001 max.	mass%
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D1160	360 max.	°C
Sodium/potassium	UOP391	5 max. combined	ppm

[a] The carbon residue shall be run on the 100% sample.

Table 7
The effects of water on biodiesel and diesel engines.

Impurity	Effects of water on biodiesel and diesel engines	Reference
Water	Major source of fuel contamination support microbial growth on tanks	[30,165,177]
	Reduce heat of combustion (less power, harder starting, more smoke)	[21]
	Corrosion of essential fuel system components fuel tubes, injector pumps fuel pumps	[21,39,152,174,177,178]
	Formation of ice crystal, providing sites of nucleation and accelerate the gelling of the residual fuel	[21]
	Speed up the growth of microbe colonies which can seriously block up a fuel system	[21,177,179,180]
	Reduces engine's useful life	[152]
	Strongly affect engine performance	[151]
	Could make biodiesel fuel go rancid and alter the chemical structure of biodiesel	[180]
	Causes a higher brake specific fuel consumption	[181]
	Deterioration of biodiesel quality	[161]

150 ppm of moisture while petro-diesel can only absorb 50 ppm of moisture. Demirbas [21] reported that the water content of biodiesel decreases the heat of combustion. In addition, as water approaches 0 °C, it may begin to form ice crystals. These crystals provide sites of nucleation and speed up the gelling of the residual fuel. The author noted that water is part of the respiration system of most microbes. Therefore presence of water accelerates hydrolytic reaction and the development of microbe colonies which can plug fuel system [21]. According to Leung et al. [170] water content in biodiesel will increase biodiesel degradation due to hydrolysis but its effect is much less when expose to high temperature and air. Further, biodiesel from waste soybean oil is the least stable. This is because the used oil has already suffered hydrolytic degradation as a result of cooking process, which destroys the oil's natural antioxidants [171]. Similarly, Srivastava and Prasad [172] noted that the problems faced with long-term storage of biodiesel are mainly hydrolytic and oxidative degradation. Hydrolytic degradation consists of hydrolysis of methyl esters when water is present in the reaction medium. The solubility and the emulsifiability in water of fuel are heavily dependent on the quality of the biodiesel product. The authors stated that biodiesel containing high content of intermediate products (mono- and diglycerides) will have the tendency to absorb water to a higher degree than biodiesel constituting mainly methyl ester [172].

Furthermore, Bondioli et al. [173] examined the storage behavior of fatty acid methyl ester produced from rapeseed oil at a temperature of 20 and 40 °C. The study of the methyl ester behavior was conducted under controlled storage conditions with different quantities of water in glass and iron vessels. The authors noted increase in peroxide and acid values for a period of 180 days. Felizardo et al. [39] noted that fuel contaminated with water can cause engine corrosion. For that reason, EN 14214 (2003) imposes a maximum water content of 0.05% in fuels. The authors noted that this technique (EN 14214 (2003)), although used in laboratory practice, but not efficient and the water content in several biodiesel samples are mostly high, ranging from 0.08% to 0.21%. They used anhydrous magnesium sulfate to dry the biodiesels produced. On an industrial scale, dewatering is usually carried out by distillation under vacuum (0.05 bar) at temperatures of 30–40 °C. Furthermore, Fazal et al. [174] noted that higher moisture absorption, presence of oxygen moieties, and fatty acids produced from auto-oxidation seemed to act as major factors to enhanced corrosiveness of biodiesel. As well, comparative bio-fuel performance in internal combustion engines was investigated by Crookes [175]. The author noted that emulsification with water can be used to further reduce the emissions. In another investigation, Sharma et al. [176] reported that purification step can destroys natural antioxidants contained in biodiesel, thereby making biodiesel susceptible to oxidation. For this reason, synthetic antioxidants such as phenolic types or aminic types have to be added to biodiesel to make it stable and acceptable in market. Table 7 shows the effects of water on biodiesel fuel and engines.

6. Conclusion and recommendation

Successful application of biodiesel fuel in diesel engines and its global replacement of petro-diesel fuel are solidly dependent on its purity and quality. Biodiesel production was found to be faced with water problems especially when low quality raw materials containing higher amount of water and FFAs contents are used. Water was found to be at the root of most of the problems faced in biodiesel production and refining processes. Thus in most conventional biodiesel production processes, refined raw materials are used otherwise the reaction could either seize to occur or result in low biodiesel yield and quality. The use of refined raw materials was viewed as impracticable in producing economically viable biodiesel fuel. Heterogeneous catalysts seemed to considerably favor biodiesel production when low quality feedstocks used, evading some problems associated with homogeneous catalysts.

Although supercritical methanol method is limited by elevated operating conditions, but its offers simpler purification process for biodiesel production involving feedstocks containing considerable amount of water and FFAs contents. In purification process, use of water has been found to be associated with wastewater discharges thereby resulting to huge amount of wastewater discharges. Also, presence of water was found to affect the quality of biodiesel fuel during storage and use on diesel engines. Therefore tremendous efforts need to be made by the scientific World to develop a sound and economically viable technologies that can deal with the effects of water on the production and refining of biodiesel, so as to make it a fuel for future.

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